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Global Management of Language-Related Projects

340 Brannan Street, Fifth Floor
San Francisco, CA 94107 • USA

Tel (415) 512-8800
FAX (415) 512-8982

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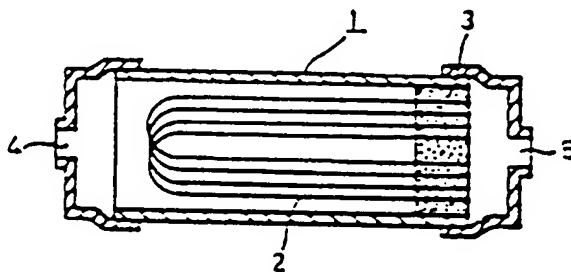
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(71) Applicant: 000006035 (Mitsubishi Rayon Co., Ltd.)
(72) Inventor: Hisayoshi Yamamori
(72) Inventor: Akiyoshi Uchida
(72) Inventor: Takeshi Kurushima
(72) Inventor: Yoshihiro Tsunomoto
(72) Inventor: Mie Isobe
(74) Agent: Tadashi Wakabayashi, Patent Attorney

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- (54) [Title of the Invention] **Method for Manufacturing Hydrophilized
Porous Membrane**

- (57) [Summary]

[Object] A method for manufacturing a hydrophilized porous membrane by securing to the surface of a polyolefin-based porous membrane an ethylene-based copolymer that serves as a hydrophilization agent, contains a hydrophilic portion, and possesses considerable affinity for polyolefin-based resins, wherein the porous membrane is endowed with an effective membrane surface area to prevent performance deterioration during use.

[Structure] A polyolefin-based porous membrane is dipped in a solution of an ethylene-based copolymer (containing at least 20 mol% ethylene units and at least 10 mol% hydrophilic monomer units) serving as a hydrophilization agent to allow said copolymer to be adsorbed on said porous membrane; draining is subsequently performed in such a way that said copolymer is deposited in an amount sufficient to render said porous membrane hydrophilic but is prevented from forming a coat; and the product is then dried.



[Claims]

[Claim 1] A method for manufacturing a hydrophilized porous membrane, characterized by comprising the steps of: (A) dipping a polyolefin-based porous membrane in a hydrophilizing solution that contains an ethylene-based copolymer containing at least 20 mol% ethylene units and at least 10 mol% hydrophilic monomer units to adsorb said copolymer on said porous membrane, (B) draining excess hydrophilizing solution from said porous membrane, and (C) drying the drained porous membrane.

[Claim 2] A method for manufacturing a hydrophilized porous membrane as defined in claim 1, wherein the amount in which said copolymer is adsorbed during step A is 1 to 10% owf.

[Claim 3] A method for manufacturing a hydrophilized porous membrane as defined in claim 1 or 2, wherein when the amount, X, in which said hydrophilizing solution is retained by the porous membrane drained during step B is expressed by

$$X (\% \text{ owf}) = \{(v \times \rho_2)\} / \{(100 - v) \times \rho_1\} \times a \quad (I)$$

(where v is the porosity of the porous membrane, ρ_1 is the density of the material (in a nonporous state) constituting the porous membrane, ρ_2 is the density of the

hydrophilizing solution, and a is a constant), step B is performed under conditions corresponding to an a value within a range of 20 to 250.

[Claim 4] A method for manufacturing a hydrophilized porous membrane as defined in any of claims 1 through 3, wherein said hydrophilic monomer units are vinyl alcohol units.

[Claim 5] A method for manufacturing a hydrophilized porous membrane as defined in any of claims 1 through 4, wherein the hydrophilizing solution contains a mixed alcohol-water solvent and said copolymer.

[Claim 6] A method for manufacturing a hydrophilized porous membrane as defined in any of claims 1 through 5, wherein the polyolefin-based porous membrane is a hollow-fiber membrane made into a porous membrane by drawing.

[Detailed Description of the Invention]

[0001]

[Field of Industrial Utilization] The present invention relates to a method for manufacturing a hydrophilized porous membrane by incorporating an ethylene-based copolymer containing ethylene units and hydrophilic monomer units into a polyolefin-based porous membrane.

[0002]

[Prior Art] Polyolefin-based porous membranes consisting of resins obtained from compositions containing olefin-based monomers as their principal components possess high chemical stability and have other advantages, and are thus widely used in medical applications, semiconductors, water purification, and a variety of other fields.

[0003] Since such polyolefin-based porous membranes are initially hydrophobic, they must be rendered hydrophilic before being used to treat aqueous fluids (fluids containing water as their principal component).

[0004] An example of a method for rendering a polyolefin-based porous membrane hydrophilic is to wet the outer surfaces of the polyolefin-based porous membrane and the inner surfaces of the micropores (hereinafter abbreviated as "the surface") with an alcohol, ketone, or other organic solvent highly compatible with water, and to subsequently substitute water for the organic solvent.

[0005] A porous membrane rendered hydrophilic by this method, however, must always be kept in contact with water to preserve the hydrophilic properties and, once dried, must be again rendered hydrophilic because of the loss of its hydrophilic properties.

[0006] There is also a method for rendering a polyolefin-based porous membrane hydrophilic by depositing a water-soluble hydrophilic macromolecule (polyethylene glycol or the like) or a hydrophilization agent (a surfactant or the like) on the surface of the membrane. During the use of a porous membrane rendered hydrophilic by this method, however, the hydrophilization agent deposited on the pore surface is readily eluted into water, and, once dried, the porous membrane in such a state loses its hydrophilic properties and must again be subjected to a hydrophilization treatment. Another disadvantage is that a comparatively large amount of the hydrophilization agent is eluted into the water being treated when a hydrophilized porous membrane obtained by this method is used, precluding the use of this membrane in applications for which such an elution of the hydrophilization agent is undesirable.

[0007] To address these problems, it has been proposed to select and deposit macromolecules that contain hydrophilic portions, possess affinity for polyolefin-based resins, and do not readily elute into the water being treated when deposited on polyolefin-based porous membranes, while taking into account the balance between the hydrophilic and hydrophobic properties displayed by the micropore surfaces of the porous membranes.

[0008] An example of this method is described in Japanese Laid-Open Patent Application 61-125408. According to this method, a thin film consisting of an ethylene-vinyl acetate copolymer is first formed on the surface of a polyethylene-based porous membrane and is then subjected to a saponification treatment.

[0009] This method, while allowing polyethylene-based porous membranes to acquire permanent hydrophilic properties, is disadvantageous because a saponification treatment must be performed following the deposition of an ethylene-vinyl acetate copolymer on the porous membrane, complicating the process.

[0010] Processes in which the saponification treatment is omitted and the procedures are simplified have therefore been studied. Japanese Laid-Open Patent Application 61-271003 describes one such method, according to which the surface of a polyolefin-

based porous membrane is coated with an ethylene-vinyl alcohol copolymer serving as an ethylene-based copolymer.

[0011] These processes involve coating the surface of a polyolefin-based porous membrane with an ethylene-vinyl alcohol copolymer by drying the polyolefin-based porous membrane after dipping it in a solution prepared by adding the ethylene-vinyl alcohol copolymer to a mixed solvent consisting of water and an organic solvent.

[0012]

[Problems Which the Invention Is Intended to Solve] A disadvantage of hydrophilized porous membranes obtained by the methods in which the porous surfaces are coated with the aforementioned ethylene-vinyl alcohol copolymers is that water permeability decreases and other parameters related to performance are often adversely affected when the product is used as a filtration membrane, for example.

[0013] The aforementioned performance deterioration has proven to be even more pronounced when such methods are used to treat hollow-fiber membrane bundles formed by bundling numerous hollow-fiber membranes, sheets formed by twisting numerous hollow-fiber membranes, and other such products.

[0014] As a result of research into these shortcomings, the inventors concluded that the aforementioned undesirable phenomena are caused by the fact that when an ethylene-based copolymer is deposited on the surface of a porous membrane by a conventional method, it becomes difficult to perform excess deposit adjustments, the micropores are clogged by the ethylene-based copolymer coat, and the micropore diameter is reduced, with the result that the effective surface area of the porous membrane decreases, the filtration capacity is reduced by the clogging of the micropores as the cumulative amount of the water being filtered increases with increased operating time, and other undesirable changes tend to occur.

[0015] It is also believed that when numerous hollow-fiber membranes are simultaneously treated in a single operation, the aforementioned effect of excess ethylene-based copolymer adhering to the micropores is enhanced by the mutual bonding of adjacent hollow-fiber membranes during the drying of the ethylene-based copolymer solution deposited on the outer surfaces of the hollow-fiber membranes, with the result that the micropores of the bonded portions cannot be effectively utilized,

adversely affecting the performance even more as the cumulative amount of the water being filtered increases with increased operating time.

[0016] As a result of painstaking research conducted in view of the above situation and aimed at overcoming these shortcomings, the inventors perfected the present invention after discovering that the desired permanent hydrophilic properties can be obtained, a reduction in filtration capacity can be prevented when the product is used to perform a filtration treatment, and the mutual bonding of adjacent hollow-fiber membranes (observed when numerous hollow-fiber membranes are simultaneously treated in one operation) is inhibited when the surface of a polyolefin-based porous membrane is coated with an ethylene-vinyl alcohol copolymer not by drying a polyolefin-based porous membrane after dipping it in a solution (prepared by adding the ethylene-vinyl alcohol copolymer to a mixed solvent containing water and an organic solvent) in a manner sufficient to merely impregnate the interior of the porous membrane with said solution, but by keeping said membrane in said solution even after the interior of the porous membrane has been thoroughly impregnated with said solution, removing said membrane from said solution and into the air after said ethylene-vinyl alcohol copolymer has been physically adsorbed on said membrane in a prescribed amount, then performing draining in such a way that said copolymer was deposited in an amount sufficient to render said porous membrane hydrophilic without forming a coat, and finally drying the product.

[0017] An object of the present invention is to offer a method for manufacturing a hydrophilized porous membrane in the course of simplified processes that can yield a hydrophilized polyolefin-based porous membrane less prone to reductions in filtration capacity and in other performance parameters.

[0018] Another object of the present invention is to offer a method for manufacturing a hydrophilized porous membrane in which the bonding of adjacent hollow-fiber membranes is less likely to occur even when numerous polyolefin-based hollow-fiber membranes are simultaneously treated in one operation.

[0019]

[Means Used to Solve the Above-Mentioned Problems] A distinctive feature of the proposed method for manufacturing a hydrophilized porous membrane is that it comprises the steps of (A) dipping a polyolefin-based porous membrane in a hydrophilizing solution that contains an ethylene-based copolymer containing at least

20 mol% ethylene units and at least 10 mol% hydrophilic monomer units to adsorb said copolymer on said porous membrane, (B) draining excess hydrophilizing solution from said porous membrane, and (C) drying the drained porous membrane.

[0020] The polyolefin-based porous membrane used in the method of the present invention is a porous membrane consisting of a polyolefin-based resin obtained from a composition containing an olefin-based monomer as the principal component. Examples of such olefin-based monomers include ethylene, propylene, 4-methyl-1-pentene, and 3-methyl-1-butene.

[0021] Examples of polyolefin-based resins include polymers obtained using a single monomer selected from among the aforementioned olefin-based monomers, and polymers obtained using two or more monomers selected from among the aforementioned olefin-based monomers.

[0022] As long as the desired characteristics of polyolefins are not compromised, these polyolefin-based resins may also be obtained by copolymerizing units obtained from monomers other than olefin-based monomers, or by introducing fluorine or various other substituent groups.

[0023] A hollow-fiber membrane, flat membrane, tubular membrane, or product of any other desired shape can be used as the porous membrane employed in the method of the present invention.

[0024] No particular restrictions are imposed on the thickness, micropore diameter, porosity, and other characteristics of the porous membrane used in the method of the present invention, and the hydrophilization treatment can be performed without adversely affecting characteristics related to the porosity or micropore diameter of the porous membrane because the method of the present invention prevents the ethylene-based copolymer serving as the hydrophilization agent from forming a coat on the surface of the porous membrane. In particular, the method of the present invention is suitable for hydrophilizing hollow-fiber membranes because the hydrophilization treatment can be performed without adversely affecting the advantages of hollow-fiber membranes, which are characterized by a considerable surface area per unit volume.

[0025] The method of the present invention makes it possible to effectively hydrophilize a suitable porous membrane such as a filtration membrane with a thickness

of about 20 to 200 μm , a porosity of about 20 to 90%, and a micropore diameter of about 0.01 to 5 μm .

[0026] The porosity of a membrane is the value defined by Formula II below

$$\text{Porosity (v, \%)} = (1 - \rho_a/\rho_1) \times 100 \quad (\text{II})$$

(where ρ_a is the apparent porosity of the porous membrane, and ρ_1 is the density (in a nonporous state) of the material constituting the porous membrane).

[0027] No particular restrictions are imposed on the type of porous membrane, and it is possible to use porous membranes with various microporous structures obtained by drawing methods (in which a material is rendered porous by being first melt-formed and then drawn), extraction methods (in which a material containing inorganic substances and other fillers removable by extraction is rendered porous by a process in which said material is melt-formed while containing the fillers, which are then extracted), and various other methods.

[0028] Of these membranes, the porous membranes obtained by the drawing methods have the following characteristics: they possess considerable porosities, are less likely to undergo functional deterioration due to clogging, and contain none of the impurities readily eluted into the water being treated. The method of the present invention allows a hydrophilization treatment to be performed without adversely affecting these characteristics, and it therefore particularly suitable for the hydrophilization of porous membranes obtained by drawing methods.

[0029] Porous membranes obtained by the drawing methods have porous-membrane structures in which slit-shape microscopic spaces (micropores) formed by microfibrils and node portions are interconnected in a three-dimensional pattern. These membranes can, for example, be manufactured by the methods described in Japanese Patent Publication 56-52123 and Japanese Laid-Open Patent Application 57-42919.

[0030] The hydrophilizing solution used in process A of the proposed method can be obtained by dissolving in a solvent an ethylene-based copolymer serving as the hydrophilization agent.

[0031] An ethylene-based copolymer containing at least 20 mol% ethylene units and at least 10 mol% (and preferably at least 20 mol%) hydrophilic monomer units can be used as the ethylene-based copolymer.

[0032] It is unsuitable for the content of ethylene units in said copolymer to be lower than 20 mol%, because in this case the copolymer does not develop adequate affinity for the polyolefin-based porous membrane, is adsorbed less readily on the porous membrane, and is apt to separate from the surface of the porous membrane during the draining treatment (step B) described below, or the hydrophilization agent is readily eluted into the water being treated during the use of the ultimately obtained hydrophilized porous membrane. Nor is it suitable for the content of hydrophilic monomer units to be lower than 10 mol%, because it becomes impossible in this case to obtain satisfactory hydrophilic properties.

[0033] The ethylene-based copolymer is not subject to any restrictions in terms of polymerization mode, so polymers obtained by random polymerization, block polymerization, graft polymerization, and various other types of polymerization can be used.

[0034] Examples of the hydrophilic monomer units contained in the ethylene-based copolymer include those obtained from monomers such as vinyl alcohol, (meth)acrylic acid, (meth)acrylates, hydroxyethyl (meth)acrylates, polyethylene glycol (meth)acrylic acid esters, vinyl pyrrolidone, acrylamides, and other vinyl compounds. These may be used individually or as combinations of two or more components.

[0035] In addition to containing the aforementioned ethylene units and hydrophilic monomer units, the ethylene-based copolymer may contain other units as long as the desired characteristics afforded by these units are not adversely affected. Examples of such other units include vinyl acetate, (meth)acrylic acid esters, vinyl alcohol fatty acid esters, compounds obtained by the formalation of vinyl alcohol, compounds obtained by the butyralation of vinyl alcohol, and other monomers.

[0036] As long as effective drying can be performed in the course of the drying treatment (step C) described below, no limitations are imposed on the use of the solvent designed to prepare the hydrophilizing solution for coating the porous membrane with the ethylene-based copolymer serving as the hydrophilization agent. Examples include mixed solvents containing alcohol and water, organic solvents such as dimethyl

formamide or dimethyl sulfonamide, and mixed solvents containing these organic solvents and water. Of these, water/ethanol mixed solvents containing 50 to 90 wt% ethanol can be cited as particularly suitable because they are highly safe for humans when used in medical or beverage applications, and because they are easy to dry due to their low boiling points.

[0037] The dipping of the polyolefin-based porous membrane in the hydrophilizing solution makes it possible to adsorb the ethylene-based copolymer contained in the hydrophilizing solution on the surface of the porous membrane. (As mentioned above, the term "the outer surface and micropore surface of the porous membrane" includes the outer surface, cavity inner surface, and micropore inner surface in the case of a hollow-fiber membranes).

[0038] The composition of the hydrophilizing solution, the dipping time of the porous membrane, the temperature, the agitation type, and other dipping conditions, although varying with the type of ethylene-based copolymer contained in the hydrophilizing solution, the type of porous membrane, the extent of treatment, and other parameters, are suitably selected to allow the draining treatment described below to be effectively performed, and to ensure that the ultimate amount in which the ethylene-based copolymer is adsorbed on the surface of the porous membrane falls within a suitable range.

[0039] The dipping conditions of the dipping treatment should, for example, be set in such a way that the value calculated using Formula III below (the value shows the ratio in which the hydrophilization agent has been deposited on the porous membrane) is about 1 to 10% owf.

$$\text{Adsorption ratio (Y}^1\text{, \% owf)} = (A_1 - A_2)/A_1 \times 100 \quad (\text{III})$$

(In the formula, A_1 is the amount in which the ethylene-based copolymer is contained in the hydrophilizing solution prior to dipping, and A_2 is the amount in which the ethylene-based copolymer is contained in the hydrophilizing solution following dipping).

[0040] The amounts in which the ethylene-based copolymer is contained in the hydrophilizing solution (these amounts are defined as A_1 and A_2) can be determined by sampling suitable amounts of hydrophilizing solutions before and after dipping,

measuring the weight of the solids remaining when the solvents have been distilled off, and calculating the total amount of solids in the hydrophilizing solution.

[0041] The dipping time can be set, for example, to 15 minutes or longer, and preferably 20 minutes or longer, to allow the hydrophilization agent to be adequately adsorbed.

[0042] The concentration of the ethylene-based copolymer in the hydrophilizing solution can, for example, be about 0.1 to 10 wt%, and preferably about 0.3 to 5 wt%. It is unsuitable for the concentration to be lower than 0.1 wt% or higher than 10 wt% because in the first case the ethylene-based copolymer cannot be adsorbed in a sufficient amount, and in the second case the ethylene-based copolymer is adsorbed in an excessively large amount, making it impossible to attain a sufficient draining effect during the subsequent draining treatment, and facilitating the clogging of the micropores in the porous membrane by the ethylene-based copolymer.

[0043] The dipped porous membrane subsequently undergoes a draining treatment (step B).

[0044] The draining treatment is performed in order to drain excess hydrophilizing solution from the surface of the porous membrane.

[0045] The draining conditions are therefore set in such a way that the amount in which the ethylene-based copolymer serving as the hydrophilization agent adheres to the surface of the porous membrane following the drying treatment described below is sufficient to render the porous membrane hydrophilic while preventing the formation of a coat. For example, effective draining can be performed by setting the conditions in such a way that the constant a determining the retention ratio X expressed by Formula I below falls within a range of 20 to 250.

$$X (\% \text{ owf}) = \{(v \times \rho_2)\} / \{(100 - v) \times \rho_1\} \times a \quad (I)$$

(In the formula, v is the porosity of the porous membrane, ρ_1 is the density of the material (in a nonporous state) constituting the porous membrane, ρ_2 is the density of the hydrophilizing solution, and a is the constant).

[0046] Excess hydrophilizing solution is effectively removed from the outer surface of the porous membrane (the outer surface and the cavity inner surface in the case of a hollow-fiber membrane) by performing the draining treatment under these conditions.

[0047] The retention ratio X of the hydrophilizing solution can be calculated by measuring the weight of the porous membrane before and after the treatment.

[0048] Examples of the draining method include a draining method in which the hydrophilizing solution is allowed to drip off under the action of gravity from the porous membrane taken out of the hydrophilizing solution, a draining method in which the hydrophilizing solution is blown off by the pressure of compressed air blown toward the porous membrane, a draining method in which the solution is allowed to drip off from the porous membrane by the application of supersonic vibrations, and a method in which the solution is drained off from the porous membrane by the action of centrifugal force.

[0049] Of these methods, the methods involving the use of centrifugal force is preferred because of the following advantages: (a) the extent of draining (the ultimate extent of adhesion of the ethylene-based copolymer) can be adjusted by varying the centrifugal conditions, (b) draining can be performed in a short time and can be accompanied by drying, and the method is devoid of disadvantages such as the retention of excess hydrophilization agent on the surface of the porous membrane, (c) effective drainage from inside the cavities is facilitated when hollow-fiber membranes are used, etc.

[0050] The magnitude of the centrifugal force applied in the case of centrifugal draining varies with the type of hydrophilizing solution used, the type of porous membrane, and other factors, but the upper limit of the centrifugal force must be set for each type of porous membrane used because the shape of the porous membrane itself can be distorted when the force is too strong. In view of this, the centrifugal force is usually set to between about 5 and 600 G.

[0051] Even when the hydrophilizing solution has penetrated nonuniformly into the porous membrane during step A, the draining treatment has the effect of eliminating this nonuniformity by allowing the hydrophilizing solution to flow during the draining treatment.

[0052] Once the aforementioned draining treatment has been completed, the porous membrane is dried during step C, making it possible to fix the ethylene-based copolymer on the surface of the porous membrane and to impart permanent hydrophilic properties to the porous membrane.

[0053] The drying treatment can be performed using vacuum drying, hot-blast drying, and various other drying methods. Temperature conditions that prevent the porous membrane from being deformed by heat, for example, a temperature of 120°C or lower, should be adopted during said drying treatment.

[0054] As described above, the amount in which the ethylene-based copolymer serving as the hydrophilization agent is deposited on the porous membrane should be sufficient to allow the hydrophilization agent to develop its effect while preventing said agent from forming a coat on the surface of the porous membrane. It is possible, for example, to set the deposition ratio (expressed as the rate of change of the weight before and after the hydrophilization treatment) to between about 1 and 40% owf, preferably about 5 and 30% owf, and ideally about 5 and 15% owf.

[0055] The ultimate ratio in which the ethylene-based copolymer is deposited on the porous membrane can be adjusted by appropriately selecting the concentration of the hydrophilizing solution, the draining conditions, and the like.

[0056]

[Practical Examples] The present invention will now be described in further detail through practical and comparative examples.

[0057] The adsorption ratio and other parameters used herein were calculated by the following methods.

[0058] (1) Ratio in Which Ethylene-based Copolymer Is Adsorbed During Dipping
(Y¹, % owf)

Suitable amounts of the hydrophilizing solution were sampled before and after dipping, the amount of the remaining solids was measured when the solvent had been distilled off from the samples, the weight of the solids contained in the entire hydrophilizing solution before and after dipping was calculated using these results, and the ratio was determined in accordance with Formula III above.

[0059] (2) Retention Ratio of Hydrophilizing Solution

The weight of a piece of knitted fabric was measured prior to dipping and following a predetermined treatment stage, and the retention ratio was calculated using Formula IV below.

$$\text{Retention ratio (X, \% owf)} = (B_2 - B_1)/B_1 \times 100 \quad (\text{IV})$$

(In the formula, B_1 is the weight of the piece of knitted fabric prior to dipping, and B_2 is the weight of the piece of knitted fabric following a predetermined post-dipping treatment stage). Of the results shown in Table 1, Practical Examples 1 through 3 concern the post-dipping retention ratios obtained by centrifugation, whereas Comparative Examples 1 and 2 concern the retention ratios obtained following stationary dripping.

[0060] (3) Value of a in Formula I Above

The value was calculated from Formula I above using the retention ratio (X) of the hydrophilizing solution calculated in Paragraph 2 above.

[0061] (4) Deposition Ratio Following Drying

The weight of a piece of knitted fabric was measured prior to the hydrophilization treatment and following the drying treatment, and the ratio was calculated using Formula V below.

$$\text{Adsorption ratio (Y}^2, \% \text{ owf)} = (C_2 - C_1)/C_1 \times 100 \quad (\text{V})$$

(In the formula, C_1 is the weight of the piece of knitted fabric prior to dipping, and C_2 is the weight of the piece of knitted fabric following drying).

[0062] (5) Amount of Water Flow

A hollow-fiber membrane module 1 with the structure shown in Figure 1 was fabricated, distilled water used to measure the amount of water flow was fed through the water feed port 4 at a water pressure of 1 kg/cm², the water was allowed to flow through the surfaces of hollow-fiber membranes 2 into the cavities and then to leave through a water discharge port 5, and the amount of water flow per unit time was measured.

[0063] (6) Retention Ratio of Water Flow

The method described in 5 above was used to measure the initial amount of water flow before filtration was performed with the aid of the hollow-fiber membrane module 1 with the structure shown in Figure 1, and after 4 m³ of Nagoya city tap water had been continuously filtered at a constant rate of 3 L/min, and the results were used to calculate the retention ratio of water flow in accordance with Formula VI below.

$$\text{Retention ratio of water flow (\%)} = D_2/D_1 \times 100 \quad (\text{VI})$$

(In the formula, D_1 is the initial amount of water flow, and D_2 is the amount of water flow following the filtration of 4 m³).

[0064] Practical Example 1

Polyethylene porous-fiber membranes (EHF 270T; manufactured by Mitsubishi Rayon; porosity: 72%, specific gravity of polyethylene (in a nonporous state) serving as a constituent material: 0.965) that had an outside diameter of 380 μm and were made into 16 double yarns were used as the weft yarn, and a polyester textured yarn (50 d/24 f) was used as the warp yarn. A jacquard raschel machine was used to manufacture a woven fabric which had a width of 120 mm and in which only the two selvages were chain-stitched with the warp yarns.

[0065] A hydrophilizing solution obtained by dissolving an ethylene-vinyl alcohol copolymer (hydrophilization agent; ethylene content: 44 mol%; manufactured by Nippon Synthetic Chemical; "Soanol A4412") at a concentration of 1.4 wt% in a mixed ethanol/water (volume ratio: 75/25) solvent was kept at a temperature of 50°C. A piece of fabric manufactured in advance was dipped in the solution for 20 minutes and then taken out.

[0066] To allow the hydrophilization agent to be uniformly adsorbed on the fabric during dipping, the solution was agitated and the fabric was lightly moved up and down in the hydrophilizing solution. The amount (Y^1) in which the hydrophilization agent was adsorbed during this dipping treatment was measured by the method described in Paragraph 1 above, and was found to be 4.9% owf.

[0067] The piece of fabric taken out of the solution was subsequently allowed to stand for about 1 minute above the dipping bath to allow the adhered solution to drip

off from the piece of fabric, thus performing a stationary dripping treatment. The retention ratio (X) of the hydrophilizing solution following this stationary dripping treatment was measured by the method described in 2 above, and was found to be 730% owf. The value of a in Formula I above was calculated on the basis of this retention ratio, and was found to be 310.

[0068] The piece of fabric was placed in a centrifuge and drained for 5 minutes with a centrifugal force of 20 G. The retention ratio (X) of the hydrophilizing solution following this dripping treatment was measured by the method described in 2 above, and was found to be 240% owf. The value of a in Formula I above was calculated on the basis of this retention ratio, and was found to be 102.

[0069] The drained piece of fabric was dried in a 60°C hot-blast drier for 30 minutes, yielding a polyethylene porous hollow-fiber membrane in which the deposition ratio (Y^2) of the ethylene-vinyl alcohol copolymer serving as the hydrophilization agent was 9.3% owf. (The deposition ratio was calculated in accordance with Paragraph 4 above).

[0070] The hollow-fiber membranes were pulled out of the piece of fabric, bundled to form a U-shape, and each fixed with a urethane resin at the two open ends in such a way that the ends remained unblocked, yielding, as shown in Figure 1, a membrane module which had an effective membrane area of 0.6 m² and possessed a structure in which the resin fixing portion 3 divided the module into the following two watertight areas: an area that was in contact with the outer surfaces of the hollow-fiber membranes 2 and was connected to the water feed port 4, and an area that was connected to the water discharge port 5 and to the cavities inside the hollow-fiber membranes 2.

[0071] The ratio in which the water flowing through this membrane module was retained was measured by the methods described in Paragraphs 5 and 6 above. The results obtained are shown in Table 1.

[0072] Practical Example 2

Porous hollow-fiber membranes were rendered hydrophilic in the same manner as in Practical Example 1 (except that the dipping time was 10 minutes), a filter module was manufactured, and the ratio in which the water passing through the module was retained was measured. The results are shown in Table 1.

[0073] Comparative Example 1

Porous hollow-fiber membranes were rendered hydrophilic in the same manner as in Practical Example 1 (except that no draining was conducted using a centrifuge), a filter module was manufactured, and the ratio in which the water passing through the module was retained was measured. The results are shown in Table 1.

[0073] Comparative Example 2

Porous hollow-fiber membranes were rendered hydrophilic in the same manner as in Practical Example 1 (except that the concentration of the hydrophilization agent was 1.3 wt%, the dipping time was 1 minute, and no draining was conducted using a centrifuge), a filter module was manufactured, and the ratio in which the water passing through the module was retained was measured. The results are shown in Table 1.

[0075] Practical Example 3

Porous hollow-fiber membranes were rendered hydrophilic in the same manner as in Practical Example 1 (except that the solution was kept at 50°C and that said solution was obtained by dissolving, at a concentration of 1.2 wt% in a mixed ethanol/water (volume ratio: 70/30) solvent, an ethylene-vinyl alcohol-vinyl acetate copolymer (molar ratio: 30:46:24; synthesized by the partial acetylation of an ethylene-vinyl alcohol copolymer in accordance with a conventional method) serving as a hydrophilizing solution), a filter module was manufactured, and the ratio in which the water passing through the module was retained was measured. The results are shown in Table 1.

[0076]

[Table 1]

	Y ¹ (% owf)	X (% owf)	a	Y ² (% owf)	Initial amount of water flow (L/min)	Retention ratio of water flow (%)
Practical Example 1	4.9	240	102	9.3	4.4	90
Practical Example	2.0		130	7.1	3.0	75
Practical Example 3	4.8	260	108	8.2	5.9	89
Comparative Example 1	4.2	730	310	14.3	4.0	42
Comparative Example 2	0.1		120	9.1	3.8	33

[0077]

[Merits of the Invention] The proposed method for manufacturing a hydrophilized porous membrane allows an ethylene-based copolymer serving as a hydrophilization agent to be deposited on the surface of a porous membrane in a suitable amount at which no copolymer coat is formed, yielding an effective membrane surface that can be used during filtration or the like while preventing the micropores from being clogged by a coat formed by excess hydrophilization agent and preventing the pore diameters from being reduced beyond the necessary level. As a result, it is possible to offer a porous membrane less apt to reduce the amount of water flow or to undergo other types of functional deterioration as the cumulative amount of the water being filtered increases with increased filtration time.

[Brief Description of the Figures]

[Figure 1] A schematic cross section showing the structure of a hollow-fiber membrane filtration module.

[Key]

1: hollow-fiber membrane filtration module, 2: hollow-fiber membrane, 3: resin fixing portion, 4: water feed port, 5: water discharge port

[Figure 1]

